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DIMERIC HYDROLYSABLE TANNINS FROM *MELASTOMA MALABATHRICUM**

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Key Word Index—*Melastoma malabathricum*; Melastomataceae; tannins; hydrolysable tannin dimer; malabathrins B, C and D.

Abstract—Three new hydrolysable tannin dimers, malabathrins B, C and D, and 11 known tannins including three dimers (nobotanins B, G and H) and a trimer (nobotanin J), have been isolated from the leaves of *Melastoma malabathricum*. The structures of new dimers were determined by spectral analysis and chemical correlations with nobotanins B and J.

INTRODUCTION

The occurrence of ellagitannins in melastomataceous plants was first demonstrated by the detection of ellagic acid in chromatographic surveys of the hydrolysates of leaf extracts of various plant species [1, 2]. However, little was known about the ellagitannins themselves in this family, until the isolation of monomeric and oligomeric ellagitannins (nobotanins A–E)§, the first fully characterized tannins, from *Tibouchina semidecandra* [3–6]. Nobotanins G–K, structurally related to nobotanin B, were also isolated from *Heterocentron roseum* [7, 8], and these oligomers were later found to be characteristic constituents in melastomataceous plants (Yoshida *et al.*, unpublished). The present paper reports the isolation of nobotanins B, G, H and J, and three new dimers from *Melastoma malabathricum*, a tree growing in Madagascar, India, Malaysia and Australia. The leaves of this plant have been used as a crude drug called 'daun harendong' in Indonesia and Malaysia, for treatment of diarrhoea, dysentery and leucorrhoea [**9**]. The main tannin of this crude drug is nobotanin B (**8**), which was recently found to exhibit potent *in vitro* antiviral activity against human immunodeficiency virus [**10**].

RESULTS AND DISCUSSION

The dried leaves of *M. malabathricum* were homogenized in 70% acetone and the concentrated homogenate subjected to column chromatography over Diaion HP-20, and to subsequent repeated column chromatography on Toyopearl HW-40 and/or MCI gel CHP-20P, to afford three new tannins, named malabathrins B (**9**), C (**14**) and D (**17**). A flavonoid glycoside (isoquercitrin 6″-*O*-gallate [11]), and 11 hydrolysable tannins were also isolated. Among the latter, seven were monomeric hydrolysable tannins, 1,4,6-tri-*O*-galloyl-β-D-glucose (**1**) [12], 1,2,4,6-tetra-*O*-galloyl-β-D-glucose (**2**) [13], strictinin (**3**), casuarictin (**4**), pedunculagin (**5**) [14], nobotanin D (**6**) [5] and pterocarinin C (**7**) [15]. The other four were hydrolysable tannin oligomers which were identified as nobotanins B (**8**) [4, 6], G (**15**), H (**16**) (dimers) [7] and nobotanin J (**18**) (trimer) [8].

Malabathrin B (**9**), $[\alpha]_D + 59°$ (MeOH), was obtained as a light brown amorphous powder and gave a positive colouration with alcoholic ferric chloride and sodium nitrite–acetic acid reagents on TLC [16]. Its ^{1}H NMR spectrum is complicated owing to formation of an equilibrium mixture of α- and β-anomers. Two pairs of aromatic 2H singlets [δ6.97, 6.96 (2H in total) and 7.25, 7.26 (2H in total)] indicated the presence of two galloyl groups. The presence of two hexahydroxydiphenoyl (HHDP) and a valoneoyl group was suggested by seven pairs of 1H singlets at δ6.11–7.09 (see Experimental). The two C1 glucopyranose residues were revealed by the coupling patterns of the aliphatic proton signals assigned with the aid of a ^{1}H–^{1}H COSY spectrum. One (glucose-I) of the glucose cores is fully acylated and its C-6 methylene protons appear at δ5.34 (5.33) (*dd*, $J = 6.5$, 13 Hz) and 3.89 (3.81) (*d*, $J = 13$ Hz). The large difference (Δδ 1.45–1.42) of the chemical shifts between each proton of the methylene groups indicates the presence of the HHDP (or HHDP part of the valoneoyl) group at O-4/O-6 of glucose-I [17]. The presence of galloyl group at O-6′ of the other glucose core (glucose-II) is shown by the chemical shifts of H-6′ signals [δ4.81 (4.95) (*br d*, $J = 13$ Hz) and 3.77 (3.74) (*br d*, $J = 13$ Hz)], which are analogous to those of **6** [5] and **7** [15]. The H-5′ signal of glucose-II resonates at a higher field [δ3.12 (3.69) (*br d*, $J = 10$ Hz)] than that (δ4.68) of glucose-I. This upfield shift of H-5′ is characteristic of nobotanins B (**8**) and G (**15**), in which the valoneoyl group is located at O-2/O-3 of a glucose core and at O-4 of the other glucose core [7]. Malabathrin B is thus a degalloyl-

*Part 4 in the series 'Tannins and Related Polyphenols of Melastomataceous Plants'. For Part 3, see Ref. [7].

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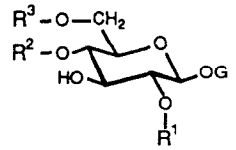
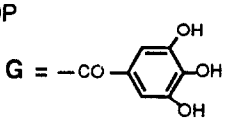
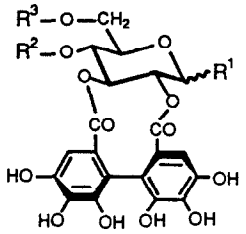
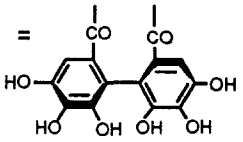
§The name 'nobotanin' is derived from 'nobotan-ka' which is the Japanese name for the family Melastomataceae.



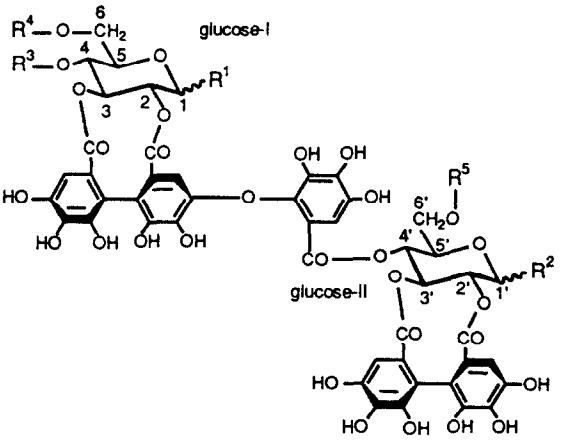
1: R^1 = H, R^2 = R^3 = G
2: R^1 = R^2 = R^3 = G
3: R^1 = H, R^2, R^3 = (*S*)-HHDP







4: R^1 = (β)-OG, R^2, R^3 = (*S*)-HHDP
5: R^1 = OH, R^2, R^3 = (*S*)-HHDP
6: R^1 = (β)-OG, R^2 = H, R^3 = G
7: R^1 = (β)-OG, R^2 = R^3 = G



	R^1	R^2	R^3	R^4	R^5
8	(β)-OG	(β)-OG	(*S*)-HHDP		G
9	(β)-OG	OH	(*S*)-HHDP		G
10	(β)-OG	OH	(*S*)-HHDP		H
11	OH	OH	(*S*)-HHDP		G
12	OH	OH	(*S*)-HHDP		H
13	OH	OH	H	H	H
14	OH	(β)-OG	(*S*)-HHDP		G

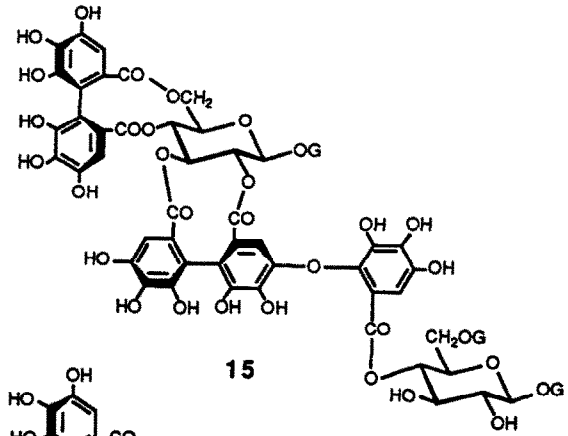
ated derivative (**9**) of nobotanin B (**8**). The FAB mass spectrum of **9**, which exhibits a $[M+Na]^+$ peak at *m/z* 1743, supported this structure.

The structure **9** of malabathrin B was substantiated by partial hydrolysis of nobotanin B (**8**) with tannase, giving a monodegalloylated derivative identical with malabathrin B (**9**), along with four other partial hydrolysates **10**–**13**. The hydrolysates **10** and **11**, which form an equilibrium mixture of two and of four anomers, respectively, were characterized as bisdegalloylated derivatives, based on their ^{1}H NMR spectra which exhibited the presence of a galloyl, a valoneoyl and two HHDP groups. Although the ^{1}H NMR spectra of the remaining two hydrolysates were complicated owing to equilibration among the four anomers, the structures **12** and **13** were assigned to these hydrolysates on the basis of number of aromatic proton signals (see Experimental).

Malabathrin C (**14**), $[\alpha]_D$ +55° (MeOH), showed a pseudo-molecular ion peak (*m/z* 1743 $[M+Na]^+$) in its FAB mass spectrum, the same as that of **9**. Although its ^{1}H NMR spectrum is complicated due to formation of an equilibrium mixture of two anomers, the presence of a valoneoyl, two galloyl and two HHDP groups in the molecule, as found in **9**, was indicated by the aromatic proton signals (see Experimental). The ^{1}H–^{1}H COSY spectrum revealed that both glucose cores in **14** adopt the C1 conformation. One (glucose-I) of the glucose cores was shown to have a HHDP group (or HHDP part of a valoneoyl group) at O-4/O-6, by a large chemical shift difference ($\Delta\delta$ 1.4) between the C-6 methylene proton signals. The hydroxyl group at the anomeric centre of this glucose was shown to be free from the chemical shift of the anomeric proton signals [δ 5.22 (J = 3.5 Hz), 5.02 (J = 8 Hz)]. The H-5′ signal of the other glucose core, whose hydroxyl groups are all acylated, was observed at δ 3.68 (*br d*, J = 10 Hz), which is very similar to that of **9**. These data indicate that this compound is a regio-isomer of **9** concerning a galloyl group. The structure **14** thus assigned was substantiated by its transformation with tannase into **12**, which was obtained by partial hydrolysis of nobotanin B (**8**) as described above.

Malabathrin D (**17**), $[\alpha]_D$ +54° (MeOH), was obtained as an off-white amorphous powder. Its ^{1}H NMR spectrum showed the presence of three galloyl groups [δ 6.97, 7.08, 7.26 (each 2H, *s*)], a HHDP group and two valoneoyl groups [δ 6.08, 6.11, 6.38, 6.45, 6.52, 6.61, 7.06, 7.10 (each 1H, *s*)], and two fully acylated C1 glucopyranose residues. These constructing units of **17** are the same as those of nobotanin H (**16**). In fact, the ^{1}H NMR spectrum of **17** was almost superimposable on that of **16** [7], except for a valoneoyl proton signal shifted to δ 6.11 and a methoxyl proton signal appearing at δ 3.63. These spectral findings and the FAB mass spectral data (*m/z* 2077 $[M+Na]^+$) indicate that malabathrin D is a methyl ester of nobotanin H (**16**). The structure **17** of malabathrin D was supported by methanolysis of nobotanin J (**18**) with a mixture of acetate buffer and MeOH (1:9), yielding **17**.

As previously reported [18], nobotanin J (**18**) is easily hydrolysed into **16** and **5**, when kept in an aqueous solution at 37° for several weeks. Malabathrin D may thus be an artefact produced from **16** or **18** during the chromatographic separation developed with aqueous methanol.



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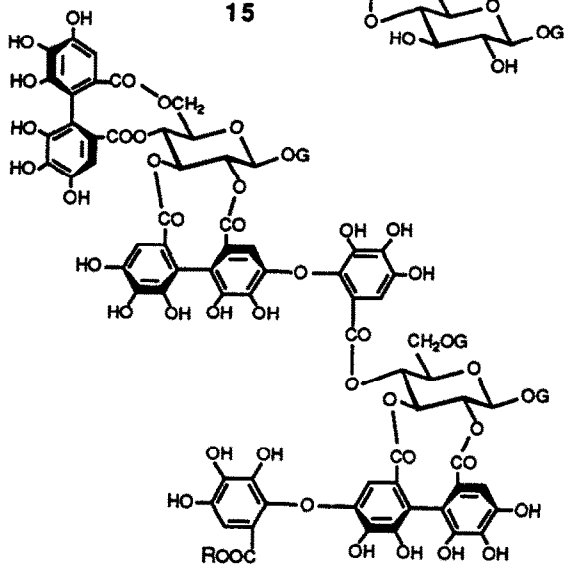
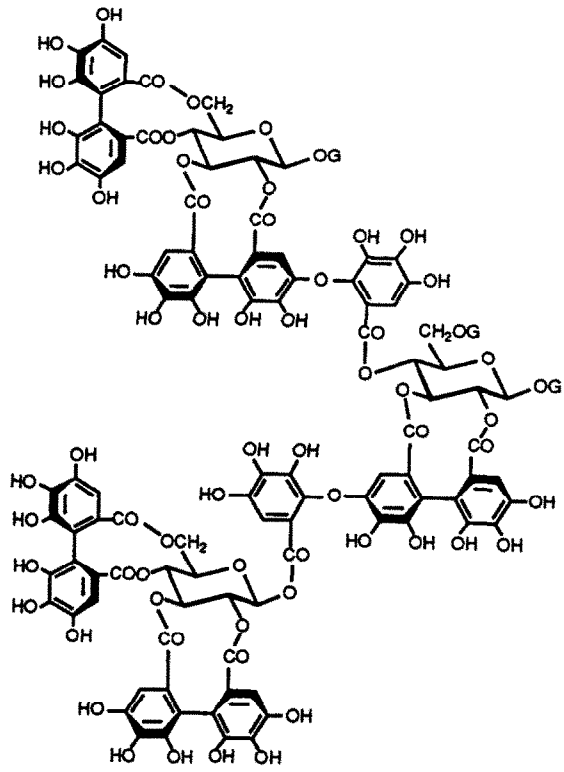


16 : R = H
17 : R = CH_3



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EXPERIMENTAL

^1H and ^{13}CNMR were recorded at 500 and 126 MHz, respectively; chemical shifts are given in δ values relative to acetone-d_6 (δ 2.04 for ^1H and δ 29.8 for ^{13}C). HPLC was conducted on Superspher Si 60 (4 mm × 119 mm) and LiChrospher RP-18 (4 mm × 250 mm) columns, using (A) hexane–MeOH–THF–HCO_2H (60:45:15:1) and oxalic acid (500 mg $l.21^{-1}$), (B) 0.05 M Pi buffer–EtOH–EtOAc (17:2:1). (C) 0.05 M Pi buffer–MeCN (17:3), (D) 0.05 M Pi buffer–EtOH–EtOAc (87:8:5), (E) 0.05 M Pi buffer–EtOH (25:2), or (F) 0.05 M Pi buffer–EtOH–EtOAc (83:12:5). CC was carried out on Toyopearl HW-40 (coarse and fine grades) (Tosoh), and Diaion HP-20 and MCI-gel CHP-20P (Mitsubishi).

Plant material. Dried leaves of *M. malabathricum* L. were purchased at a market in Sukabumi, Cap Lonceng, Indonesia, in August 1988, and identified by comparison with the dried authentic plant specimens at Herbarium Bogoriense. A voucher specimen (AN-SKJ No. 283) is deposited at the Faculty of Pharmaceutical Sciences, Kyoto University.

Isolation of tannins. Dried leaves (5 kg) were homogenized in 70% aq. Me_2CO and the homogenates filtered. The concd filtrate was subjected to CC over Diaion HP-20 eluting with H_2O containing increasing amounts of MeOH to give 9 frs [I (H_2O eluate; 85 g), II (10% MeOH eluate; 3.6 g), III (30% MeOH eluate-1; 5.3 g), IV (30% MeOH eluate-2; 9.8 g), V (40% MeOH eluate-1; 10 g), VI (40% MeOH eluate-2; 9 g), VII (50% MeOH eluate-1; 10 g), VIII (50% MeOH eluate-2; 5.4 g) and IX (60% MeOH eluate; 8.2 g)]. Fr. IV was further chromatographed over Toyopearl HW-40 (coarse) with 70% MeOH to give strictinin (**3**) (680 mg) and peduculagin (**5**) (226 mg). Fr. VI was subjected to a combination of chromatography over Toyopearl HW-40 (coarse) [60% MeOH→70%MeOH→MeOH–Me_2CO–H_2O (7:2:1)] and MCI-gel CHP-20P (H_2O→20% MeOH→30% MeOH→40% MeOH) to give 1,4,6-tri-*O*-galloyl-β-D-glucose (**1**) (192 mg), nobotanin D (**6**) (580 mg), malabathrins B (**9**) (125 mg) and C (**14**) (15 mg), and nobotanins G (**15**) (46 mg) and H (**16**) (29 mg). Fr. VII was similarly rechromatographed over Toyopearl HW-40 (coarse) to yield 1 (175 mg), nobotanins D (**6**) (118 mg), B (**8**) (907 mg), G (**15**) (471 mg) and H (**16**) (95 mg), and malabathrin D (**17**) (27 mg). Repeated CC of fr. VIII over Toyopearl HW-40 (coarse) and MCI-gel CHP 20P afforded isoquercitrin 6″-*O*-gallate (83 mg), 1,2,4,6-tetra-*O*-galloyl-β-D-glucose (**2**) (41 mg), pterocarinin C (**7**) (251 mg), nobotanins B (**8**) (400 mg), G (**15**) (84 mg) and J (**18**) (211 mg).

Malabathrin B (**9**). Light brown amorphous powder. $[\alpha]_D$ +59° (MeOH; *c* 1.0). (Found: C, 50.91; H, 3.74. $C_{75}H_{52}O_{48}\cdot 3H_2O$ requires: C, 50.62; H, 3.52%.) FABMS *m/z*: 1743 $[M+Na]^+$, 1759 $[M+K]^+$. CD (MeOH) [θ] (nm): +19

$\times 10^4$ (235), -7.0×10^4 (261), 2.2×10^4 (284), -2.1×10^4 (314). ^{1}H NMR [$(CD_3)_2CO$–D_2O]: δ6.97, 6.96 (each *s*, 2H in total), 7.25, 7.26 (each *s*, 2H in total) (galloyl), 6.12, 6.13 (each *s*, 1H in total), 6.37, 6.38 (each *s*, 1H in total), 6.43, 6.44 (each *s*, 1H in total), 6.55, 6.57 (each *s*, 1H in total), 6.62 (*s*, 1H), 6.63, 6.64 (each *s*, 1H in total), 7.09, 7.07 (each *s*, 1H in total) (hexahydroxydiphenoyl and valoneoyl); (α-anomer), 6.20 (*d*, J = 8.5 Hz, H-1), 5.11 (*dd*, J = 8.5, 9.5 Hz, H-2), 5.75 (*dd*, J = 9.5, 10 Hz, H-3), 5.13 (*t*, J = 10 Hz, H-4), 4.68 (*dd*, J = 6, 10 Hz, H-5), 5.34 (*dd*, J = 6, 13 Hz, H-6), 3.88 (*d*, J = 13 Hz, H-6), 5.41 (*d*, J = 3.5 Hz, H-1'), 5.03 (*dd*, J = 3.5, 9.5 Hz, H-2'), 5.60 (*t*, J = 9.5 Hz, H-3'), 5.69 (*t*, J = 9.5 Hz, H-4'), 3.74 (*br d*, J = 10 Hz, H-5'), 3.82 (*dd*, J = 1, 13 Hz, H-6'), (β-anomer), 6.20 (*d*, J = 8.5 Hz, H-1), 5.11 (*dd*, J = 8.5, 9.5 Hz, H-2), 5.78 (*dd*, J = 9.5, 10 Hz, H-3), 5.14 (*t*, J = 10 Hz, H-4), 4.68 (*dd*, J = 6, 10 Hz, H-5), 5.33 (*dd*, J = 6, 13 Hz), 3.89 (*d*, J = 13 Hz, H-6), 4.79 (*d*, J = 8 Hz, H-1'), 4.85 (*dd*, J = 8, 9.5 Hz, H-2'), 5.23 (*t*, J = 10 Hz, H-3'), 5.70 (*t*, J = 10 Hz, H-4'). 3.12 (*br d*, J = 10 Hz, H-5'), 3.77 (*br d*, J = 13 Hz, H-6').

Malabathrin C (**14**). Light brown amorphous powder. $[\alpha]_D$ +55° (MeOH; *c* 1.0). (Found: C, 49.01; H, 3.61. $C_{75}H_{52}O_{48} \cdot 6H_2O$ requires: C, 49.23; H, 3.50%.) FABMS *m/z*: 1743 $[M+Na]^+$. CD (MeOH) [θ] (nm): $+22 \times 10^4$ (236), -8.8×10^4 (263), $+2.7 \times 10^4$ (284), -2.9×10^4 (312). ^{1}H NMR [$(CD_3)_2CO + D_2O$]: δ7.20, 7.16 (each *s*, 2H in total), 7.09, 7.08 (each *s*, 2H in total) (galloyl), 7.15 (1H, *s*), 6.60, 6.62 (each *s*, 1H in total), 6.58, 6.51 (each *s*, 1H in total), 6.48, 6.49 (each *s*, 1H in total), 6.45, 6.42 (each *s*, 1H in total), 6.33, 6.34 (each *s*, 1H in total), 6.03, 6.02 (each *s*, 1H in total); (α-anomer): δ5.22 (*d*, J = 3.5 Hz, H-1), 4.95 (*dd*, J = 3.5, 8 Hz, H-2), 5.52 (*t*, J = 10 Hz, H-3), 5.02 (*t*, J = 10 Hz, H-4), 4.31 (*dd*, J = 6.5, 10 Hz, H-5), 5.23 (*dd*, J = 6.5, 12.5 Hz, H-6), 3.83 (*d*, J = 12.5 Hz, H-6), 6.04 (*d*, J = 8.5 Hz, H-1'), 5.11 (*dd*, J = 8.5, 10 Hz, H-2'), 5.34 (*t*, J = 10 Hz, H-3'), 5.63 (*t*, J = 10 Hz, H-4'), 3.68 (*br d*, J = 10 Hz, H-5'), 4.81 (*br d*, J = 13 Hz, H-6'), 3.80 (*br d*, J = 13 Hz, H-6'); (β-anomer): δ5.02 (*d*, J = 8 Hz, H-1), 4.79 (*t*, J = 8 Hz, H-2), 5.56 (*br t*, J = 10 Hz, H-3), 5.03 (*t*, J = 10 Hz, H-4), 4.31 (*dd*, J = 6.5, 10 Hz, H-5), 5.23 (*dd*, J = 6.5, 12.5 Hz, H-6), 3.83 (*d*, J = 12.5 Hz, H-6), 6.02 (*d*, J = 8.5 Hz, H-1'), 5.17 (*dd*, J = 8.5, 10 Hz, H-2'), 5.42 (*t*, J = 10 Hz, H-3'), 5.80 (*t*, J = 10 Hz, H-4'), 4.81 (*br d*, J = 13 Hz, H-6'), 3.80 (*br d*, J = 13 Hz, H-6').

Malabathrin D (**17**). Off-white amorphous powder. $[\alpha]_D$ +54° (MeOH; *c* 1.0). (Found: C, 50.35; H, 3.77. $C_{90}H_{62}O_{57} \cdot 5H_2O$ requires: C, 50.37; H, 3.36%.) CD (MeOH) [θ] (nm): $+24 \times 10^4$ (225), $+1.8 \times 10^4$ (235), -8.6×10^4 (260), $+1.7 \times 10^4$ (281), -2.2×10^4 (308). FABMS: *m/z* 2077 $[M+Ma]^+$. ^{1}H NMR [$(CD_3)_2CO$–D_2O]: δ6.15 (*d*, J = 8.5 Hz, H-1), 5.09 (*dd*, J = 8.5, 9 Hz, H-2), 5.82 (*t*, J = 9 Hz, H-3), 5.12 (*t*, J = 9 Hz, H-4), 4.63 (*dd*, J = 6, 9 Hz, H-5), 5.28 (*dd*, J = 6, 13 Hz, H-6), 3.89 (*d*, J = 13 Hz, H-6), 5.99 (*d*, J = 8.5 Hz, H-1'), 5.16 (*dd*, J = 8.5, 9 Hz, H-2'), 5.32 (*t*, J = 9 Hz, H-3'), 5.72 (*t*, J = 9 Hz, H-4'), 4.87 (*d*, J = 13 Hz, H-6'), 3.78 (*d*, J = 13 Hz, H-6'), H-5' overlapped with DHO signal, 3.64 (3H, *s*, OMe); aromatic protons see text.

Partial hydrolysis of nobotanin B (**8**) *with tannase*. A soln of nobotanin B (**8**) (86 mg) in H_2O (42 ml) containing tannase (0.3 ml) [19] was incubated for 18 hr at 37°. The reaction mixt. was concd and applied to an MCI-gel CHP-20P column in H_2O. Elution with H_2O containing increasing amounts of MeOH (10%→20%→25%→30%→40%) gave gallic acid (11 mg), **9** (6.5 mg), **10** (6 mg), **11** (6.5 mg), **12** (12 mg) and **13** (3 mg). The hydrolysate **9** was identified as malabathrin B by HPLC co-chromatography (normal and reverse-phase) and ^{1}H NMR spectral comparison. Compound **10**: ^{1}H NMR [$(CD_3)_2CO$–D_2O]: 7.05, 7.04 (each *s*, 2H in total, galloyl), 6.13, 6.15 (each *s*, 1H in total), 6.34, 6.35 (each *s*, 1H in total), 6.39, 6.40 (each *s*, 1H in total), 6.55, 6.57 (each *s*, 1H in total), 6.59, 6.58 (each *s*, 1H in total), 6.62 (*s*, 1H), 6.97, 7.0 (each *s*, 1H in total) (hexahydroxydiphenoyl and valoneoyl); (α-anomer) 6.10 (*d*, J = 8.5 Hz, H-1), 5.08 (*dd*, J = 8.5, 10 Hz, H-2), 5.40 (*dd*, J = 9, 10 Hz, H-3), 5.09 (*t*, J = 9 Hz, H-4), 4.41 (*dd*, J = 6.5, 9 Hz, H-5), 5.27 (*d*, J = 6.5, 13 Hz, H-6), 3.80 (*d*, J = 13 Hz, H-6), 5.38 (*d*, J = 3.5 Hz, H-1'), 4.96 (*dd*, J = 3.5, 10 Hz, H-2'), 5.53 (*t*, J = 10 Hz, H-3'), 5.25 (*t*, J = 10 Hz, H-4'), 3.88 (*m*, H-5'); (β-anomer), 6.05 (*d*, J = 8.5 Hz, H-1), 5.08 (*dd*, J = 8.5, 10 Hz, H-2), 5.47 (*dd*, J = 9, 10 Hz, H-3), 5.09 (*t*, J = 9 Hz, H-4), 4.41 (*dd*, J = 6.5, 9 Hz, H-5), 5.27 (*dd*, J = 6.5, 13 Hz, H-6), 3.80 (*d*, J = 13 Hz, H-6), 4.89 (*d*, J = 8 Hz, H-1'), 4.77 (*dd*, J = 8, 10 Hz, H-2'), 5.15 (*t*, J = 10 Hz, H-3'), 5.26 (*t*, J = 10 Hz, J = 10 Hz, H-4'), H-5' and H-6' are overlapped by H_2O signal at δ3.2–3.60. Compound **11**: ^{1}H NMR [$(CD_3)_2CO$–D_2O]: δ7.19, 7.13, 7.17, 7.16 (each *s*, 2H in total, galloyl), 6.02, 6.11 (each *s*, 1H in total). 6.31. 6.32, 6.33 (each *s*, 1H in total), 6.41, 6.42, 6.45, 6.46 (each *s*, 1H in total), 6.52, 6.54 (each *s*, 1H in total), 6.59, 6.61, 6.62 (each *s*, 1H in total), 6.62, 6.63, 6.64 (each *s*, 1H in total), 7.05, 7.08, 7.11, 7.14 (each *s*, 1H in total) (hexahydroxydiphenoyl and valoneoyl). Compound **12**: ^{1}H NMR [$(CD_3)_2CO$–D_2O]: δ6.10, 6.104, 6.11, 6.12 (each *s*, 1H in total), 6.30, 6.31, 6.32 (each *s*, 1H in total), 6.40, 6.41, 6.42, 6.43 (each *s*, 1H in total), 6.51, 6.53, 6.55, 6.56 (each *s*, 1H in total), 6.58, 6.59 (each *s*, 1H in total), 6.61, 6.62 (each *s*, 1H in total), 7.05. 7.06, 7.07, 7.09 (each *s*, in total) (hexahydroxydiphenoyl and valoneoyl). Compound **13**: ^{1}H NMR [$(CD_3)_2CO$–D_2O]: δ6.09, 6.10. 6.12 (each *s*, 1H in total), 6.39, 6.40, 6.42 (each *s*, 1H in total), 6.56, 6.57 (each *s*, 1H in total), 6.62, 6.63, 6.633, 6.64 (each *s*, 1H in total), 7.01, 7.04, 7.05, 7.09 (each *s*, 1H in total) (hexahydroxydiphenoyl and valoneoyl).

Partial hydrolysis of malabathrin C (**14**). Malabathrin C (**14**) (0.5 mg) was treated with tannase as described above. HPLC analysis (reverse-phase; solvent D) of the reaction mixt. after 5 hr showed the formation of gallic acid (R_t 3.27 min) and a product identical with the hydrolysate **12** (R_t 2.45, 3.57, 4.02 and 4.43 min). Their identity was further confirmed by a different solvent system (solvent E) by HPLC.

Partial hydrolysis of nobotanin J (**18**). A soln of nobotanin J (**18**) (60 mg) in 0.1 M acetate buffer (pH 6)–MeOH (1:9) (50 ml) was left standing at 37° for 24 hr. Evapn of solvent gave a brownish residue, which was chromatographed over MCI-gel CHP-20P. Elution with 10% MeOH gave pedunculagin (**5**) (14 mg); the 40% MeOH eluate afforded malabathrin D (**17**) (14 mg).

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